Removal of Mercury from Waste Gas Using Bromine Gas and Aqueous Gas Absorbers

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Mercury exists in trace amounts in fossil fuels[1]. Through combustion, mercury vapor can be released to the atmosphere, where it can remain aloft for months[2], spreading over vast regions of the globe[3]. Once the mercury has deposited on land or water, it can be transformed[4] by microbial into methylmecury. Mercury poisoning from the exposures to methylmercury in fish have been documented[5]. Among human activities, coal fired power plants represent a major mercury emission source[6,7]. Today, however there is no commercially available technology that can consistently and cost-effectively capture mercury from coal-fired power plants[6,8,9]. Here we report a new approach involving the use of bromine gas (Br_2) to rapidly and selectively oxidize trace amounts of elemental mercury (Hg^0) in the presence of a relatively large quantity of SO_2, NO, and/or CO in the flue gas. The oxidized mercury and the unreacted Br_2 can subsequently be captured by alkaline solutions in a wet SO_2 scrubber. A preliminary cost estimate of this new approach is very favorable.

Regulations on mercury emissions from coal-fired power plants are imminent. Although technologies for the control of mercury emissions on sources such as waste incinerators are available, they cannot be readily applied to coal-fired power plants as the flue gas conditions are different[8]. A large amount of work[10-13] is under way to design and develop new systems for the control of mercury emission from coal-fired power plants, but to date none has been shown to provide widely effective control at acceptable cost[6,8,14].

Mercury exiting the stack of coal-fired boilers, on the order of several parts per billion (ppb), is primarily gas-phase elemental (Hg^0) and oxidized forms, with a small fraction present in the particulate phase[15]. It has been demonstrated[16] that wet SO_2 scrubbers can remove oxidized mercury quite efficiently but have little or no effect on Hg^0. Attempts[17-19] have been made to increase the oxidized fraction of mercury in the flue gas, but so far none has been found satisfactory due to high cost, slow oxidation rate, and/or lack of selectivity in the oxidation.

Kinetic studies of some gaseous reactions of Hg^0 have been performed mainly in the interest of understanding its atmospheric transport and chemistry[20-23]. It is recognized that rate determination is difficult because Hg^0 easily adsorbs on solid surfaces and the extent of the adsorption is dependent on concentration, temperature, and surface properties, as well as flow rate. In the study reported here, cold vapor atomic absorption spectroscopy (CVAAS) was used to study the reaction of Hg^0 with Br_2 under the effect of various flue gas compositions. The reaction was performed in a 330 ml Pyrex double-jacket thermostat cell equipped with two quartz windows having an optical path of 15 cm. The kinetics was performed using the absolute rate technique under pseudo-first-order condition with respect to Hg^0. Initially, the reaction cell was evacuated by a vacuum system. Then, 254 Torr of nitrogen was introduced into the cell. A known concentration of Hg^0-saturated nitrogen with or without SO_2, NO, H_2O, and/or CO was expanded into the cell to reach a pressure of 380 Torr. The Br_2 in nitrogen was then

introduced into the cell to a pressure of 508 Torr before the pressure was quickly brought to 760 Torr by adding nitrogen. The Hg^0 concentration was monitored at 253.7 nm continuously by CVAAS during the course of the reaction.

Care was taken to study the wall effect; however, the Hg^0 adsorption rate observed on the wall was small (Fig. 1) compared to the Hg^0 oxidation rate by Br_2 under all conditions employed. The reaction rate of Hg^0 with Br_2 appeared to exhibit a gradual increase with successive runs. The acceleration of the rate could be attributed to the enhanced adsorption of Hg^0 on the mercuric bromide particulate that accumulated on the cell wall. The reaction rates were in good agreement within experimental uncertainty, if the cell was carefully cleaned prior to each run.

Fig. 1 shows the results of time dependent Hg^0 oxidation rate by Br_2 under various gas compositions at 21°C and 50°C. The initial concentrations of Hg^0 and Br_2 were 0.18 ppm and 17 ppm, respectively. The half life (50% conversion) of Hg^0 with Br_2 in nitrogen was about 11.7 sec. The presence of 3000 ppm SO_2 only slightly inhibited the Hg^0 oxidation rate, increasing the half life to 13.8 sec. This increase is attributed to the concurrent reaction[24] of Br_2 with SO_2. There was no detectable change in Hg^0 oxidation rate with 200 ppm NO in the gas. The reaction of Br_2 with NO is slow because it involves a three-body collision process[25]. Unexpectedly, we found that CO increased the Hg^0 oxidation rate by Br_2. The Hg^0 half life decreased to 5.5 sec in the presence of 40 ppm CO. The oxidation rate of Hg^0 by Br_2 in a simulated flue gas containing 3000 ppm SO_2, 200 ppm NO, and 40 ppm CO was also studied. The half life of Hg^0 was measured to be 5.5 sec at 21°C and 3.0 sec at 50°C. The CO appeared to exert a major role in the oxidation of Hg^0 by Br_2 in a simulated flue gas.

Fig. 2 summarizes the rate constant and the apparent rate constants of the reaction of Hg^0 with Br_2 under various conditions. The rate constants were calculated from the kinetic

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measurements, such as those shown in Fig. 1. Each point represents an experimental run at the specific condition indicated. The average reaction rate constant determined for Hg^0 with Br_2 in nitrogen was 1.3×10^{-16} cm^3/molecule-sec at 21°C and 1.7×10^{-16} cm^3/molecule-sec at 50°C. The apparent reaction rate constants of Hg^0 with Br_2 at 21°C were 1.1×10^{-16}, 1.3×10^{-16}, 2.7×10^{-16}, and 1.2×10^{-16} cm^3/molecule-sec with 3000 ppm SO_2, 200 ppm NO, 40 ppm CO, and 24 Torr of H_2O vapor, respectively. The apparent rate constant of the reaction of Hg^0 with Br_2 in a simulated flue gas composition, containing 3000 ppm SO_2, 200 ppm NO, 40 ppm CO, and the balance nitrogen was 2.7×10^{-16} and 5.2×10^{-16} cm^3/molecule-sec at 21°C and 50°C, respectively. We have also determined the oxidation rate constants of Hg^0 with Cl_2, I_2, and HNO_3 at 21°C to be 2.6×10^{-18}, 7.3×10^{-16}, and 1.1×10^{-19} cm^3/molecule-sec, respectively. The Cl_2 and HNO_3 are not effective. Although the rate constant with I_2 is large, its low solubility, high reagent costs, and lack of selectivity in oxidation diminish its usefulness.

The fate of un-reacted Br_2 and its reaction products in flue gas must be addressed. Br_2 hydrolyzes rapidly to form hydrogen-bromide (HBr) and -hypobromite (HBrO) upon contact with aqueous solutions in SO_2 scrubbers. However, the reaction products include mercuric bromide (HgBr$_2$), sulfuryl bromide[24] (SO$_2$Br$_2$), and possibly nitrosyl bromide[25] (NOBr). The SO$_2$Br$_2$ hydrolyzes[26] to form HBr and sulfuric acid (SO$_3$•H$_2$O). The NOBr is unstable[26] and decomposes to yield NO and Br_2. All of the aforementioned products are in relatively small quantities, are highly water soluble, and will be captured in wet SO_2 scrubbers to form the corresponding alkaline salts. It is expected that compliance with current and proposed USEPA emission standards [27, 28] can be readily achieved.

The removal efficiency of the mercury and the cost of its removal are two major considerations for the implementation of a technology. An estimate of the removal efficiency and cost is underway. We assumed[6,9] that flue gas contains 3 ppb of mercury with 60% of which initially in Hg^0 and 40 % in oxidized form and that 90% removal

efficiency of the oxidized mercury by a wet SO_2 scrubber is achieved. The percentage of Hg^0 oxidized depends on the rate constant, reaction time, and Br_2 concentration employed. The rate constants of Hg^0 with Br_2 that we measured ranged between 1.0×10^{-16} and 5.2×10^{-16} cm^3/molecule-sec, depending on the gas composition and temperature (Fig. 2). The flue gas composition and conditions vary from plant to plant. In this estimate, we used a rate constant of 2×10^{-16} cm^3/molecule-sec. Typically, flue gas from the burner of a coal-fired power plant passes sequentially through a super heater, economizer, air heater, and ESP/baghouse before entering a wet SO_2 scrubber. Here, we consider the case when Br_2 is introduced to the flue gas at the air heater. The flue gas residence time is 0.5 sec - 1 sec in the air heater and 8 sec - 15 sec in an ESP or baghouse. Therefore, a total reaction time of 8.5 to 16 sec is available. The mercury removal efficiency was calculated with four Br_2 concentrations: 20, 30, 40, and 50 ppm. Fig. 3 shows that the removal efficiency increases with the increases of the reaction time and Br_2 concentration. A 70 % removal efficiency can be achieved in 10 sec with 20 ppm Br_2, but in only 3.7 sec with 50 ppm Br_2. An 80 % removal efficiency can be obtained in 10.8, 8, and 6.2 secs with a Br_2 of 30 ppm, 40 ppm, and 50 ppm, respectively. The mercury removal efficiency shown here would increase if the removal efficiency of the oxidized mercury by wet SO_2 scrubbers is larger than the assumed 90%. The cost of mercury captured is dependent on the amount of Br_2 used. Longer reaction time leads to a higher fraction of Hg^0 oxidized for a given Br_2 concentration. For a Br_2 cost[29] of $0.6/lb, 20 ppm Br_2, a 15-second reaction time, and an overall removal efficiency of 80%, it would cost approximately $4,000 per pound of mercury removed. If only an 8-second reaction time is available, 40 ppm Br_2 would need to be used for an 80% efficiency, doubling the cost to $8,000 per pound of mercury removed. Currently, powdered activated carbon (PAC) injection is the most promising method as a near-term mercury control technology despite some unsettled issues[14]. Baseline cost estimate[14] for PAC technology are in the range of $50,000 to $70,000/lb mercury captured. Therefore,

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the cost of the Br_2 oxidation approach is approximately an-order of magnitude cheaper than that of PAC. Scale-up test is warranted to demonstrate the technology for commercialization.

References

1.   Davidson, R.M., Clarke, L. Trace elements in coal. IEAPER/21, London, UK, IEA Coal Research, 60 pp (Jan., 1996).

2.   United Nations Environment Programme (UNEP), Global Mercury Assessment, UNEP Chemicals, Geneva, Switzerland (December 2002).

3.   Schroeder, W.H., Munthe, J. Atmospheric mercury – an overview. Atm. Environ., **32**, 809-822, (1998).

4.   Warner, K., Roden, E., Ongo, A. Microbial mercury transformation in anoxic freshwater sediments under iron-reducing and other electron-accepting. Environ. Sci. & Technol. **37**, 2159-2165 (2003)

5.   U.S. EPA. Mercury Study Report to Congress, EPA-452/R-97-003, Vol. I: Executive Summary (December 1997).

6.   Sloss, L.L. Mercury – emissions and control. CCC/58, ISBN 92-9029-371-3, London, UK, IEA Coal Research, 43pp (Feb., 2002)

7.   Wang, Q., Shen, W., Ma, Z. Estimation of mercury emissions from coal combustion in China. Environ. Sci. & Technol., **34**(13), 2711-2713 (2000).

8.   U.S. EPA. Mercury Study Report to Congress, EPA-452/R-97-010, Vol. VIII: An evaluation of mercury control technologies and costs, (December 1997).

9.   U.S. EPA. Control of mercury emissions from coal-fired electric utility boilers: Interim report including errata dated 3-21-02, EPA-600/R-01-109 (April 2002).

10. Bustard, J. et. al. Full-scale evaluation of sorbent injection for mercury control on coal-fired power plants. In Proceedings of Air Quality III: Mercury, Trace Elements, and Particulate Matter Conference, Arlington, VA, September 9-12, 2002.

11. Miller, S. et. al. Mercury control with the advanced hybrid. In Proceedings of Air Quality III: Mercury, Trace Elements, and Particulate Matter Conference, Arlington, VA, September 9-12, 2002.

12. McLarnon, C. Mercury removal in a multi-pollutant control technology for utility boilers. In Proceedings of Air Quality III: Mercury, Trace Elements, and Particulate Matter Conference, Arlington, VA, September 9-12, 2002.

13. Blythe, G., Richardson, C., and Rhudy, R. Pilot evaluation of the catalytic oxidation of mercury for enhanced removal in wet FGD systems. In Proceedings of Air Quality III: Mercury, Trace Elements, and Particulate Matter Conference, Arlington, VA, September 9-12, 2002.

14. Feeley, T.J., Murphy, J., Hoffmann, J., and Renninger, S.A. Review of U.S. DOE/NETL's mercury control technology R&D program for coal-fired power plants. Environ. Manag. Sept. 2003; or www.netl.doe.gov

15. Research Triangle Institute. U.S. National Mercury Emission Inventory Database, June 2001.

16. Babcock & Wilcox Company and McDermott Technology, Inc. Full-scale restings of enhanced mercury control technologies for wet FGD systems. Final report to the U.S. Department of Energy under Contract No. DE-FC26-00NT41006, August 30, 2002.

17. Granite, E.J., Pennline, H.W. Photochemical removal of mercury from flue gas. Ind. Eng. Chem. Res., 41, 5470-5476 (2002)

18.   Zhao, L.L., and G.T. Rochelle. Mercury Absorption in aqueous hypochlorite. Chem. Eng. Sci., **54**, 655-662 (1999)

19.   Kobayashi, T. Oxidation of metallic mercury in aqueous solutions by hydrogen peroxide and chlorine. J. Jpn. Soc. Air Pollut. **22**, 230 (1987)

20.   Hall, B. The gas phase oxidation of elemental mercury by ozone. Water, Air, and Soil Pollution. **80**, 301-315 (1995)

21.   Hall, B., Schager, P., and Ljumgstrom, E. An experimental study on the rate of reaction between mercury vapor and gaseous nitrogen dioxide. Water, Air, and Soil Pollution, **81**, 121-134 (1995)

22.   Tokos, J. S., Hall, B., Calhoun, J.A., and Prestbo, E.M. Homogeneous gas-phase reaction of Hg^0 with H_2O_2, O_3, CH_3I, and $(CH_3)_2S$: Implications for atmospheric Hg cycling. Atm. Environ. **32**, 823-827 (1998)

23.   Ariya, P.A., Khalizov, A., and Gidas, A. Reactions of gaseous mercury with atomic and molecular halogens: kinetics, product studies, and atmospheric implications. J. Phys. Chem. A 106, 7310-7320 (2002)

24.   Sotiropoulou, V., Katsanos, N.A., Metaxa, H., Roubani-Kalantzopoulou, F. Gas chromatographic determination of rate constants in bimolecular gaseous reactions. Chromatographia, **42**, 441-450 (1996)

25.   Hippler, H., Luu, S.H., Teitelbaum, H., Troe, J. Flash photolysis study of the NO-catalyzed recombination of bromine atoms. Int. J. Chem. Kinet., **10**, 155 (1978)

26.   Cotton, F. A., Wilkinson, G. Advanced Inorganic Chemistry – A Comprehensive Text. Second edition, P. 355 and 555, Interscience Publishers, A division of John Wiley & Sons, New York (1967)

27.   U.S. EPA R.E.D. Facts EPA-738-F-93-023 (1993)

28.   U.S. EPA National Advisory Committee for Acute Exposure Guideline Levels (AEGLs) for Hazardous Substances, OPPT-2002-0027; FRL-7189-8, Federal Register, 68 (138), 42717-42718, July 18, 2003.

29.   Chemical Market Reporter. October 21, 2002. pp 35-37.

Figure captions

Fig. 1. Conversion of elemental mercury to oxidized mercury by Br_2 under various gas compositions at $20^{\circ}C$, except the one in a simulated flue gas at both $21^{\circ}C$ and $50^{\circ}C$.

Fig. 2. Rate constants of Hg^0 with Br_2 under various conditions: Experiments used 0.18 ppm Hg^0 and 17 ppm Br_2, except B and C using 34 and 51 ppm Br_2, respectively. Additional gases are 40 ppm H_2O in E; 24 torr H_2O in F; 2000, 3000, and 5000 ppm SO_2 in G,H, and I, respectively; 200 ppm NO in J; 3000 ppm SO_2, 300 ppm NO, and 40 ppm H_2O in K; 40, 60, and 200 ppm CO in L, M, and N, respectively; 3000 ppm SO_2, 60 ppm CO, 300 ppm NO, and 40 ppm H_2O in O and P. D and P at $50^{\circ}C$, otherwise at $21^{\circ}C$.

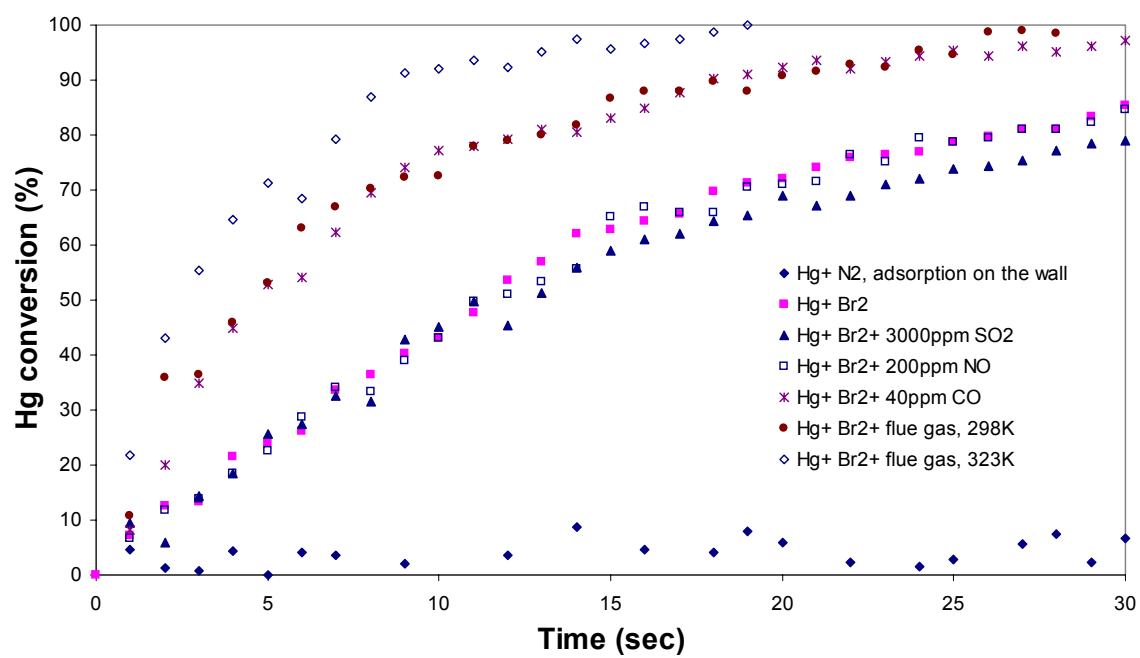Fig. 3. Mercury removal efficiency as a function of reaction time using 20, 30, 40, and 50 ppm Br_2.
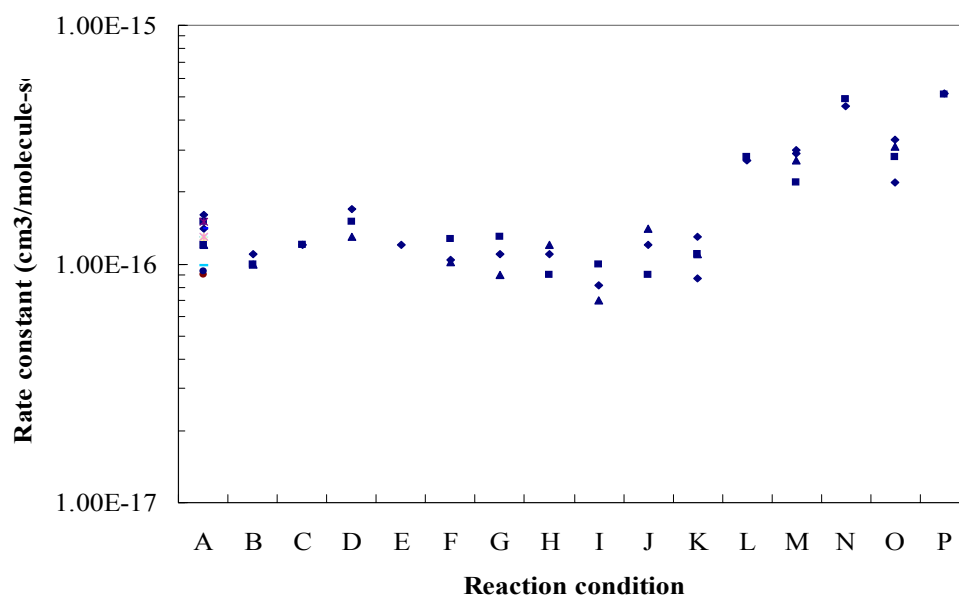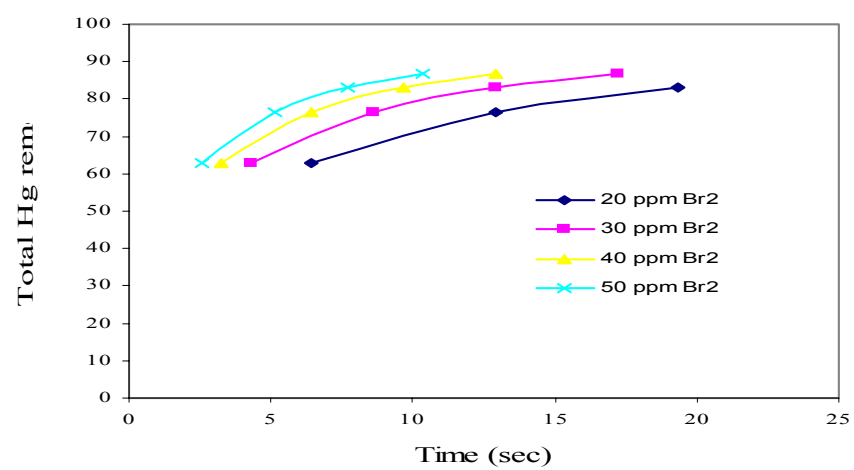
Figure 1.

Figure 2.

Figure 3.